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THE GEOCHEMISTRY OF ORGANIC SUBSTANCES OF SUBTERRANEAN WATERS

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V. M. Shvets

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THE GEOCHEMISTRY OF ORGANIC SUBSTANCES OF SUBTERRANEAN WATERS

V. M. Shvets

ABSTRACT. Sources of entry of organic substances into subterranean waters are illuminated in the article. Pathways of conversion of the organic substances into the water-soluble state and the composition, content, and principles of distribution of organic substances in subterranean waters are examined.

In recent years, a great deal of work has been done in the field of developing new methods of analyzing water soluble organic substances [4, 5, 8, 18, 20, 21], which in its turn has made it possible to use factual data to solve various geological problems. These include the following: the formation of the chemical composition of subterranean waters, ore formation, the geochemistry of abundant elements and trace elements in subterranean waters, the formation of idustrial (iodobromine) waters, the balneological significance of mineral waters, a sanitary assessment of fresh subterranean waters, petroleum formation and the petroleum-exploratory significance of subterranean waters, etc. [1, 2, 3, 6, 7, 9, 11, 12, 13, 20, 26, 27, 28].

This article is devoted to an examination of problems of the geochemistry of organic substances of subterranean waters, based on

systematizing the processing of the factual material accumulated at VSYeGINGEO since 1954.

1. Sources of Entry of Organic Substances into Subterranean Waters

V. I. Vernarskiy showed many times that water is in dynamic equilibrium with various bodies of an inorganic nature and also with aquatic organisms, microorganisms, and surface vegetation [10]. Therefore, the problem of the origin of organic substances of subterranean waters should be viewed in close interrelationship with the organic substances of various natural objects — surface waters and atmospheric precipitation, sea water and silt solutions, rocks and interstitial solutions, the topsoil, and surface vegetation.

The analysis of the content and composition of organic substances in different kinds of natural waters, soils, rocks, and silts shows that an extensive gamut of various organic compounds exists within all of these natural objects. These are primarily the various organic acids (aliphatic, humic, naphthenic, etc.), amino acids, bitumins (oils, waxes, resins, fats), phenols, humus substances, etc. The presence of the same organic compounds in various natural objects indicates the intimate relationship of the substances migrating between them, as well as the commonality of the initial organic products. Approximately the same groups and classes or organic substances and even individual organic compounds (Table 1) are in the different natural waters.

The total content of organic material in soil, rocks, and natural waters fluctuates within broad limits (Figure 1). Judging by its quantitative characteristics, one can consider its main sources for subterranean waters to be the soils (soil solutions) and rocks (Figure 2). In the infiltrative stages of the history of subterranean waters, both these sources supplement each other, since sedimentation waters do not have the capacity of enrichment of surface and ground organic material, and primarily utilize the "sea" material

TABLE 1. CONTENT AND COMPOSITION OF ORGANIC SUBSTANCES IN NATURAL WATERS*

Organic substances (waters)	Atmospheric precipitation	Dry land surface waters	Soil solutions	Sea and ocean waters	Silt Solutions	Interstitial (rock) solutions	Subterranean waters, mg/l
C_{org}, mg/l	0.8-3.4	1 - 30	4 - 30	1.0-6.3	3/8-62.6	3.63-117.8	0.1->200 (nonvolatile) Up to 100's (volatile)
N_{org}, mg/l	-	0.1	0.2-1.2	0.1-0.4	0.12-8.35	-	0.1 - 10.6
P_{org}, mg/l	-	-	-	0.004-0.034	-	-	0.03-9.0
Proteins, µg N/l	Up to 100	Up to 1000	Present	Present	-	-	-
Fats, mg/l	-	0.2-0.8	Present	Present	-	-	-
Carbohydrates, mg/l	0.23-4.0	0.07-1.0	Present	Present	Present	-	Present
Amino acids, µg N/l	4-37	2-25	Present	2.3-45.7	Present	-	0.07-2.42
Amines, µg N/l	35-73	6-100	-	-	-	-	0.01-0.46
Fatty acids, mg/l	2-18	Up to tenths	5.7-44	Up to 1	Present	Present	Up to 1000's
Fulvic acids, mg/l	-	Up to 1	Up to 1000's	-	-	-	Present
Humic acids, mg/l	-	Up to 1	Up to 1000's	-	-	-	Present
Naphthenic acids, mg/l	-	-	-	-	-	-	Up to 100's
Phenols, mg/l	-	-	Present	-	-	-	0.15-14.0
Benzene, mg/l	-	-	-	-	-	-	0.01-8.0

(Table continued on following page)

TABLE 1. (continued)

Organic substances (waters)	Atmospheric precipitation	Dry land surface waters	Soil solutions	Sea and ocean waters	Silt solutions	Interstitial (rock) solutions	Subterranean waters, mg/l
Toluene, mg/l	-	-	-	-	-	-	0.07-24.0
Bitumin, mg/l	-	-	-	-	-	-	1 - 250
Complex esters, μg · equiv/l	27-35	10-200	Present	-	-	-	Present
Alcohols, mg/l	-	-	-	Present	-	-	-
Formalin, mg/l	0.11	-	-	0.009	-	-	-
Acetone, mg/l	-	-	-	0.017	-	-	-
Acetaldehyde, mg/l	-	-	-	0.008	-	-	-
Furfurol, μg/l	-	-	-	Up to 150	-	-	-
Vitamins	-	Present	Present	Present	-	-	-
Enzymes	-	Present	Present	Present	-	-	-
Antibiotics	-	Present	Present	Present	-	-	-
Pigments	-	Present	Present	Present	-	-	-
Uronic acids	-	-	-	Present	-	-	Present
Terpenes	-	-	-	-	-	-	Present
Porphyrins	-	-	-	-	-	-	Present
Purines, pyrimidines	-	-	-	-	-	-	Present

*According to data from the literature.

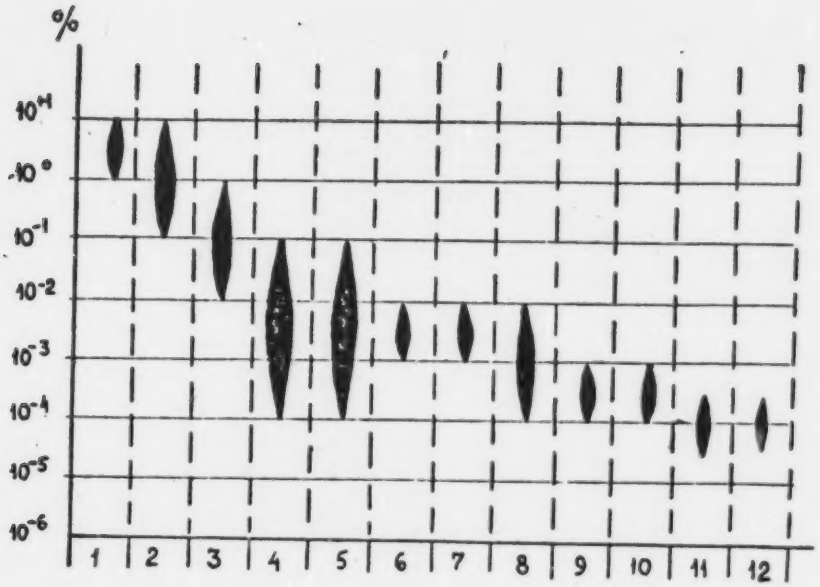

Figure 1. The content of organic material in different natural objects:

1 — soils; 2 — sea and ocean silts; 3 — rocks; 4 — subterranean waters; 5 — soil solution; 6 — interstitial solutions; 7 — aqueous rock extract; 8 — silt solutions; 9 — Aqueous petroleum extract; 10 — dry land surface waters; 11 — sea waters; 12 — atmospheric precipitation

— silts and sedimentary rocks. Petroleum deposits unquestionably facilitate the concentration of the organic material in the waters associated with them.

2. Pathways of Migration of Organic Substances into Subterranean Waters

Some of the organic substances enter the subterranean water in "ready form", and may be preserved in it for a long time. These are primarily the chemically and biologically stable compounds of the humus substances, phenols, hydrocarbons, etc. Another, unstable part is the product of complex physico-chemical and biochemical conversions. It should be emphasized that the organic material significantly differs from the mineral compounds in its mobility and capacity to participate in various, occasionally extremely rapid,

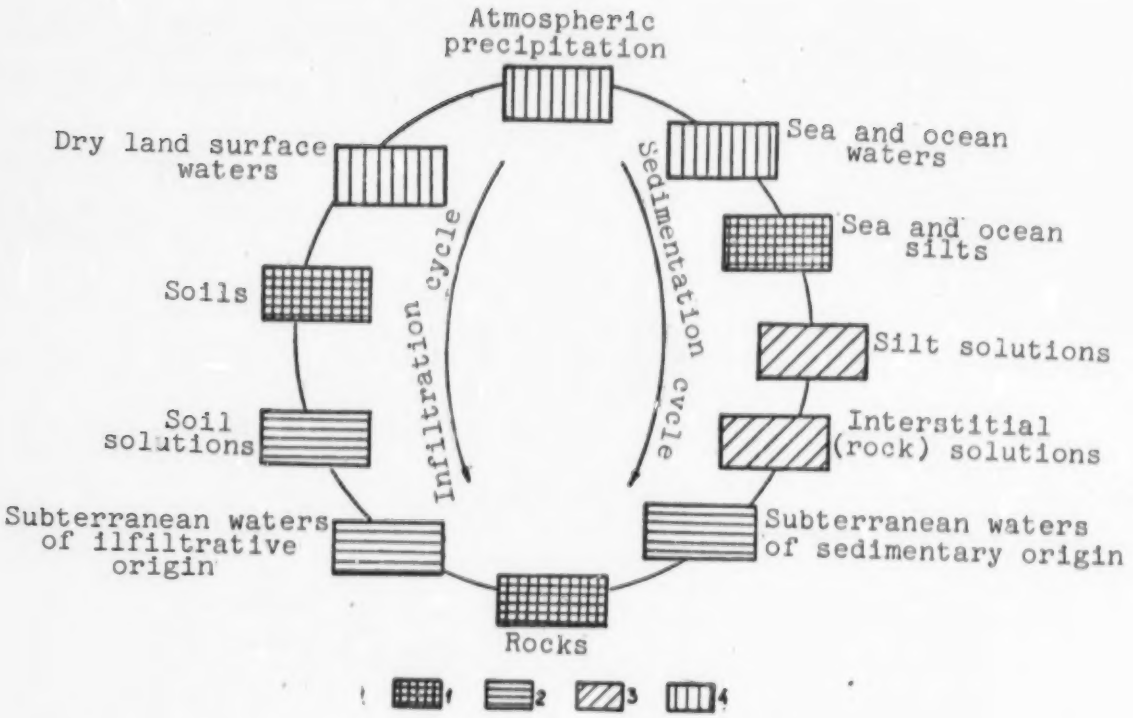

Figure 2. The interrelationship of organic substances of different natural objects. Content of organic substances in %: $1 - n \cdot 10^{-1} - 1 \cdot 10^{1}$; $2 - n \cdot 10^{-1} - n \cdot 10^{-1}$; $3 - n \cdot 10^{-1} - n \cdot 10^{-2}$; $4 - n \cdot 10^{-1} - n \cdot 10^{-3}$

processes. Moreover, it is more subject to the effect of "living material" which, in a number of cases, determines the metamorphization of organic material, under certain conditions leading to complete destruction (to conversion into the simplest terminal products — carbon dioxide and water), and under other conditions — to the formation of extremely complex compounds (hydrocarbons).

Besides the organic substances listed in Table 1 and entering the subterranean waters, it is particularly necessary to take note of the organic material of the soils. The latter was recognized by V. I. Vernadskiy, indicating that: "meteoric water, which has penetrated the soil and subsequently runs further and deeper, through the springs and streams into the river basins or the subterranean water strata is already sharply altered in its composition

in comparison with the meteoric ... water. A partial case of such a change is also the organic material which is concentrated in the water and which is developed in the soil solution" [10, p. 321]. According to the scheme of I. V. Tyurin [25], a certain role is played by "washout" of part of the humin substances and intermediate products of decay of the original organic remnants in the processes of transformation of the organic material in soil.

Gravitation water of the soils, leaching downward under the effect of the force of gravity and forming the subsoil ground waters has primary significance for the subterranean waters. The composition of the water soluble organic substances of the soil solution (Table 1) includes individual organic materials — the metabolic products of animals, plants, and microorganisms, as well as the products of their decay and the specific high molecular humus substances [17].

It may be considered proven that the migration of products of dry land life to the subterranean waters occurs through the infiltration of atmospheric, surface, and soil waters in the infiltrative stages of the history of subterranean waters. In the sedimentation stages, organic substances of marine origin enter the subterranean waters, together with silt waters. Unfortunately, the organic material in the silt waters has been very poorly studied [23]. The C_{org} content of these waters comprises approximately a few tens of milligrams per liter. Even less data are available on the organic material of the interstitial solutions [14, 15].

The migration of organic material from rocks has an extremely important significance for the waters of infiltrative and sedimentary origins. Three primary groups of organic materials are identified in rocks — bitumin, the humic acids, and residual (undissolved) organic material. The largest amount of dispersed organic material is in the clays (0.9%), and the least amount — in sands and carbonate rocks (0.2%).

The primary pathways of migration of the organic material from rocks to the subterranean water is solution. This is evinced by natural observations and experimental investigations on the solution of the organic material of rocks by distilled water, artificial solutions, and — to a lesser extent — by natural subterranean waters [16, 24]. Experiments have shown that an increase in temperature, pressure, and carbon dioxide saturation of waters leads to activation of the solution process. Experiments with natural subterranean water led to the conclusion that a bilateral interaction exists between the rock and water. The interaction is probably regulated by the relationships of concentrations and values of adsorption and consists in the migration of certain organic substances from the rocks to the water, and in others from water to the rock [3].

Petroleum deposits exert a significant effect on the geochemical situation of the subterranean regions and the enrichment of waters of petroleum-gas deposits with organic substances. It is known that the fraction of hydrocarbons in petroleum averages 92%. The remainder is made up by resins and asphaltenes, as well as other acids, sulfur and nitrogen compounds, such as the naphthenic acids (0.5%), the aromatic, aliphatic, and other acids, phenols (0.05), porphyrins, etc. [15].

Experimental investigations have shown that liquid hydrocarbons are water soluble to one degree or another. For example, at 20°, benzene dissolves in the amount of 180 mg per 100 g water, and toluene — 47 mg per 100 g water. With the increase in temperature, the solubility of hydrocarbons rapidly increases. The same phenomenon is observed upon adding solubilizers to water (the phenomenon of colloid solubility). Proportional to the increase in molecular weight of normal liquid hydrocarbons, their solubility decreases — under normal conditions, the high molecular hydrocarbons are practically insoluble in water. At the same time, the accumulations of organic material in the form of coal probably play no significant role in their enrichment of the subterranean waters, due to its high metamorphization.

Hence, one should consider that the primary pathways of migration of the organic materials to the subterranean waters are migrations from the surface of the ground in the infiltration stages, from the marine basins in the sedimentation stages, and dissolving from rocks and petroleum.

3. The Content and Distribution of Organic Substances in Subterranean Waters

We obtained a large number of analyses of different components of the organic material of subterranean waters. These are primarily quantitative data on C_{org} and N_{org}, various organic acids, phenols and benzenes, and also data on the qualitative capillary-fluorescent analysis. During the field investigations, information was obtained on the most varied waters: ground and deep artesian waters spread throughout the various physico-geographic situations, and linked with varied geological conditions, lying in the water-bearing strata of different ages and lithologic compositions, distributed throughout the petroleum-bearing and non-petroleum-bearing regions, productive (with respect to petroleum-gas deposits) and nonproductive strata, etc. In this regard, all of the factual material was grouped in accordance with the geological and hydrogeological prerequisites into four primary groups (Table 2).

Table 2 is a summary of all the available data on organic substances of subterranean waters of different regions of their extent and formation. Based on these data, a diagram (Figure 3 has been drawn. The analysis of Table 2 and Figure 3 shows the following. The quantitative content of organic substances (C_{org} total) is expressed by the total C_{org} of the three basic classes of substances — nonvolatile (C_{org}), volatile neutral (C_{org} volatile), and volatile acid (C_{org} acid). This expression of the general total of water soluble organic substances showed that earlier, during the determination of C_{org} of the nonvolatile organic substances alone, only

TABLE 2. ORGANIC SUBSTANCES OF SUBTERRANEAN WATERS OF DIFFERENT REGIONS OF FORMATION

Organic substances (and their indices)	Ground waters			Interstratum artesian waters outside petroleum-gas deposits			Subterranean waters of petroleum-gas deposits															Subterranean waters of unstressed regions		
							Petroleum deposit post-edge waters			Petroleum deposit unproduc. strata			Petroleum deposit pre-edge waters			Gas-condensate deposit pre-edge waters			Gas deposit pre-edge waters					
	n	x̄	Extent, %	n	x̄	Extent, %	n	x̄	Extent, %	n	x̄	Extent, %	n	x̄	Extent, %	n	x̄	Extent, %	n	x̄	Extent, %	n	x̄	Extent, %
C_{org}, mg/l	308	3,6	100	319	4,1	100	86	15,4	100	68	13	100	343	26,5	100	10	58,6	100	57	7,6	100	215	8,6	100
C_{org} (volatile), mg/l	28	21,1	100	29	34	100	15	25	100	14	12	100	28	95	100	5	267	100	1	5,5	—	45	35,9	100
C_{org} (acid) mg/l (calculated)	—	2,7	—	—	10,4	—	—	70	—	—	35	—	—	250	—	—	500	—	—	22	—	—	8	—
C_{org} (table), mg/l (calculated)	—	27,4	—	—	48,5	—	—	110	—	—	60	—	—	370	—	—	826	—	—	35	—	—	52,5	—
N_{org}, mg/l	183	0,33	100	217	1,25	100	36	0,60	100	29	0,64	100	157	1,20	100	—	—	—	37	0,68	100	69	0,68	100
C_{org} : N_{org}	180	13	—	210	24	—	36	23	—	29	18	—	149	40	—	—	—	—	36	18	—	68	24	—
O_2 approximate : C_{org}	190	0,5	—	103	0,4	—	45	0,7	—	1	0,5	—	150	0,7	—	—	—	—	34	1,0	—	69	0,9	—
Aliphatic acids, volatile with water vapor (mg/l)	12	6,7	58	155	60	58	16	196	69	22	93	63	35	510	82	5	959	100	8	44	75	30	25,6	70
Organic acids (direct method (mg/l)	45	6,7	88	127	26	93	13	152	100	26	67	100	20	487	100	5	1096	100	2	44,7	100	41	20,1	100
High molecular acids (mg/l)	40	0,09	65	35	0,15	71	17	0,5	58	22	0,04	41	44	0,2	36	13	0,1	31	2	0,05	100	49	0,12	61

(Table continued on following page)

TABLE 2. (continued)

Organic substances (and their indices)	Ground waters			Interstratum artesian waters outside petroleum gas deposits			Subterranean waters of petroleum-gas deposits															Subterranean waters of unstressed regions		
							Petroleum deposit post-edge waters			Petroleum deposit unproduc. strata			Petroleum deposit pre-edge waters			Gas-condensate deposit pre-edge waters			Gas deposit pre-edge waters					
	n	n'	Extent, %	n	n'	Extent, %	n	n'	Extent, %	n	n'	Extent, %	n	n'	Extent, %	n	n'	Extent, %	n	n'	Extent, %	n	n'	Extent, %
Naphthenic acids (turbidimetric method (mg/l)	180	1,9	34	169	1,3	38	38	6.6	58	30	1,4	66	91	4,1	66	—	—	—	30	0,5	66	77	2,3	67
Phenols (mg/l)	18	1,1	50	108	1,2	46	8	0,6	62	20	1,0	95	13	3,0	25	—	—	—	6	2,4	100	37	0,45	59
Luminescent substances (% of total)	273	55	100	281	52	99	56	50	100	69	52	100	273	37	97	13	57	100	35	40	89	124	57	100
Humus	273	19	95	281	19	88	56	22	87	69	19	81	273	24	81	13	26	100	35	19	77	124	19	97
Acid resins	273	17	78	281	16	63	56	13	57	69	13	64	273	13	53	13	16	100	35	16	43	124	14	71
Neutral Resins	273	4	19	281	7	28	56	5	19	69	7	27	273	3	13	13	—	—	35	3	2	124	—	—
Oils	273	4	21	281	4	22	56	8	37	69	5	21	273	15	53	13	1	13	35	19	77	124	9	36
Hydrocarbons	273	1	10	281	2	11	56	2	1	69	4	22	273	8	21	13	—	—	35	3	1	124	1	4
Naphthenic acids																								

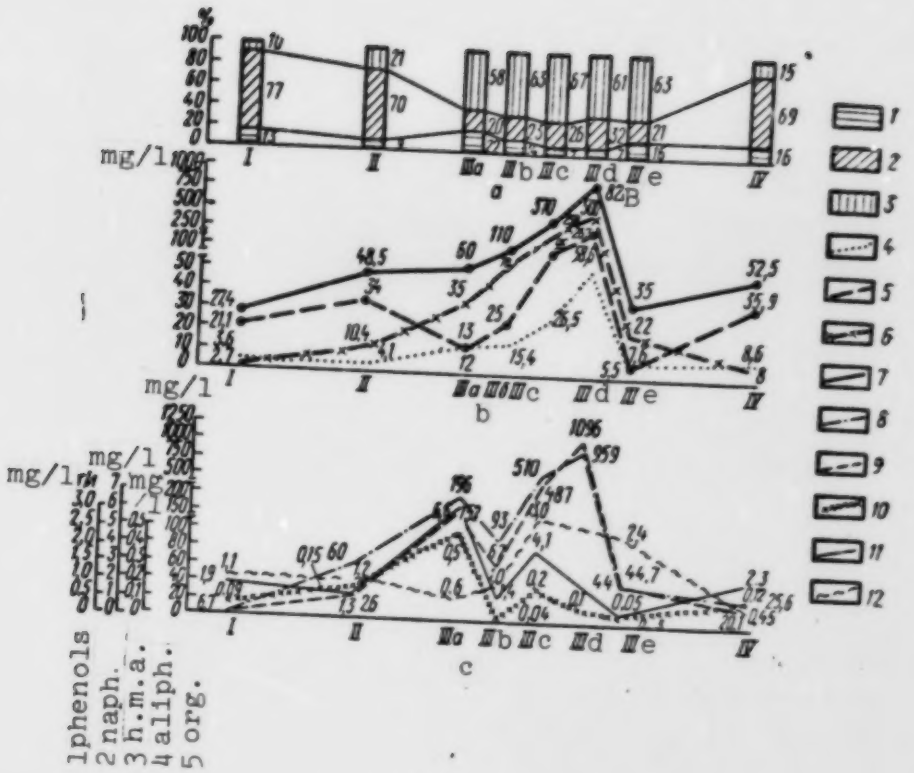

Figure 3. Change in the composition and content of organic substances in subterranean waters of different regions of formation:

a — ratio of organic substances of different classes (nonvolatile, volatile neutral, and volatile acid); b — mean content of C_{org}; c — mean content of various acids in phenols;

I — ground waters of the feeder regions; II — interstratal artesian waters outside petroleum-gas deposits; IIIa — waters of nonproductive strata of petroleum deposits; IIIb — edge waters of petroleum deposits; IIIc — edge waters of petroleum deposits (leading edge); IIId — waters of gas condensate deposits; IIIe — waters of gas deposits;

1 — nonvolatile organic substances; 2 — volatile neutral organic substances; 3 — volatile organic acids; 4 — C_{or} ; 5 — C_{org} (volatile); 6 — C_{org} (acid); 7 — C_{org} (total); 8 — aliphatic acids, volatile with water vapor; 9 — organic acids (tr. method); 10 — high molecular acids; 11 — naphthenic acids (turbidimetric method) (mg/l) 12 — phenols

naph — naphthenic acids (turbidimetric method); hma — high molecular acids; aliph — aliphatic acids; org — organic acids

7 - 22% (in different waters) of the organic material was taken into account (Figure 3). The new data make it possible to estimate differently the quantitative content and composition of the organic material of different waters. It should primarily be noted that the subterranean waters contain significantly more organic material than was earlier known. Thus (according to the average data), C_{org} (total) in ground waters of 27.4 mg/liter, reaches 48.5 in the interstratal artesian waters outside petroleum-gas deposits, and is 52.5 mg/liter in the waters of unstressed regions. Hence, an increase of almost twofold in the content of organic substances is observed, proportional to the movement of subterranean waters to a depth of up to 3 km. This increase proceeds uniformly as the result of an increase in the content of all three classes of organic materials (in mg/gl):

C_{org}: 3,6 → 4,1 → 0,6,

C_{org} (volatile): 21,1 → 34,0 → 35,0,

C_{org} (acid): 2,7 → 10,4 → 8,0.

Due to the uniform increase in C_{org} of different classes, the ratio between these classes in all three groups of waters remains nearly identical: C_{org} 9 - 16%, C_{org} (volatile) 69-77%, and C_{org} (acid) 10 - 21%.

As is apparent from Figure 3, the basic proportion of the organic material in all waters outside the petroleum-gas deposits is made up of volatile neutral compounds. These include the volatile esters, the volatile low molecular alcohols (ethyl, methyl, propyl), the hydrocarbons (termenes, benzene, and other aromatic hydrocarbons), the volatile amines, etc.

The maximum concentration of organic material occurs in the peripheral waters of the petroleum and gas condensate deposits, where C_{org} (total is*, repsectively, 370 and 826 mg/liter. Slightly

* Here and later - average values.

less organic material is in the edge waters of petroleum deposits (110 mg/liter), and still less in waters of the gas deposits (35 mg/liter). Additionally, notwithstanding the sharp difference in the C_{org} content in various waters of the petroleum-gas deposits, the nature of the organic material of these waters is obviously identical. This is indicated by the practically identical ratios of the three classes of organic substances: C_{org} 7 - 22%, C_{org} (volatile) 20 - 32%, and C_{org} (acid) 58 - 67%. Hence, the entire group of waters of the petroleum-gas deposits significantly differs from the other waters in the predominance of organic acids in their composition. In this regard, it is appropriate to recall the opinion of V. I. Vernadskiy, who wrote that the specific chemical composition of the subterranean waters of petroleum-gas deposits is related to the presence within them of dissolved organic acids, specifically, the aliphatic acids.

As the data of Table 2 and Figure 3 show, the organic acids are widespread throughout all of the subterranean waters, and it is in fact the aliphatic acids which are distinguished by maximum prevalence and high content. The high molecular acids, including the naphthenic acids, are in significantly smaller amounts. Thus, if in the edge waters of petroleum deposits there is an average of about 500 mg/liter aliphatic acids, then their found content of naphthenic acids is 4, and that of the high molecular ones — 0.2 mg/liter.

It is important to note that the content of organic low molecular acids increases in the deep waters prevalent outside the petroleum-gas deposits, in comparison with the ground waters. Thus, their quantity (mg/liter) and prevalence (shown in brackets in the ground artesian waters and waters of the unstressed region varies in the following way: organic acids — vapor distillation method — 6.7 (58%) → 60 (58%) → 25,6 (70%) ; direct method — (93%) → 20,1 6,7 (88%) → 26 (100%). It is interesting that there is somewhat less acid in waters of regions of supply than in the deep interstratal waters, which indicates processes of acid accumulation occurring in the deep waters.

With respect to the high molecular acids, their behavior in the three examined groups of waters (outside the petroleum-gas deposits) is the following: naphthenic acids — 1,9 (34%) → 1,3 (38%) → 2,3 (67%) ; high molecular acids — 0,09 (65%) → 0,15 (71%) → 0,12 (61%) . As we see, the content of these acids in the ground waters, artesian waters, and waters of unstressed regions is practically identical. It changes slightly (toward an increase) in the waters of petroleum-gas deposits Approximately the same distribution in the three groups of waters is observed for the phenols: 1,1 (50%) → 1,2 (46%) → 0,5 (59%). The phenol content of the waters of the petroleum deposits increases quantitatively only in the edge waters of petroleum (3.0 mg/liter) and gas (2.4 mg/liter) deposits, while it remains low (0.6 - 1.0 mg/liter) in the edge waters and waters of unproductive strata.

According to the data of the fluorescent analysis (Table 2), one can see the comparative constancy in the composition of luminescent organic substances — the humus substances predominate among them (as well as the alcohol resins) of isobuty. extraction, comprising 37 - 57%, and the acid resins — 19 - 24%. In this case, the minimum amount of humus substances is noted in the edge waters of the petroleum and gas deposits (37 - 40% of the total). The greatest content in prevalence of hydrocarbons is also characteristic for the same waters — 15 - 19% and 53 - 77%, respectively.

It is interesting that a more or less identical ratio of the various luminescent substances is preserved in all of the groups of waters, with the exception of the edge waters of the petroleum, gas, and gas condensate deposits: humus, 50 - 57%; acid resins, 12 - 22%; nuetral resins, 13 - 17%; oils 4 - 7%; hydrocarbons, 4 - 9%, and acids, 1 - 4%. This constancy of the ratios probably indicates stability of the indicated groups of organic substances in waters of different situations. But it is only the petroleum gas deposits which affect the change of this relationship toward an increase in hydrocarbons in the waters and a decrease in the humus substances.

A comparative estimate of the N_{org} content in the different waters shows that nitrogen accumulates in these waters proportional to their metamorphization and movement to the deep sections of the stratisphere: if N_{org} in the ground waters is maintained in the amount of 0.33 mg/liter, then in most of the deep water nitrogen increases to 0.60 - 0.68, and in the interstratal and edge waters of the petroleum deposits — to 1.20 - 1.25 mg/liter. However, the amount of nitrogenous compounds is maximum in the ground waters (C_{org} : N_{org} = 13), and minimum in the edge waters of the petroleum deposits (C_{org} : N_{org} = 40). The least acidity of the organic material (O_2 app : C_{org} more than 0.6) is a distinguishing characteristic of the ground and interstratal waters outside the petroleum-gas deposits and of the waters of the nonproductive strata of petroleum deposits.

We have already shown the comparatively low change in the percentage content of nonvolatile organic substances (in comparison with the total sum) in all of the studied waters — 7 - 22% (Figure 3). As is known, this class of nonvolatile substances includes the resins, the humus compounds, the bitumins (hydrocarbons, oils), the high molecular organic acids, phenols, carbohydrates, amino acids, etc. Most of these substances have been determined quantitatively in the waters. As an examination of the change in the values of their content in different waters shows, they are actually quite persistent in the subterranean waters and may be attributed to the constantly present stable group of water soluble organic compounds. Less stable are the volatile organic compounds which are subject to significant changes, including the aliphatic acids, whose content varies from 0 to 3500 mg/liter.

Problems of the conversions of organic substances in subterranean waters are some of the most complex. M. Ye. Al'tovskiy gave them a great deal of attention. He considered that the profound physico-chemical changes which the organic material of subterranean waters undergoes are simultaneously accompanied by complexation of

the biochemical activity of the microflora [2, 3]. Actually, according to the data of Z. I. Kuznetsova, who studied the microflora of waters during our joint investigations, an extensive gamut of aerobic and anaerobic groups of bacteria develop in subterranean waters: saprophytic bacteria, saprophytes, the sulfate-reducing bacteria, the nitrate-reducing bacteria, the cellulose-associated bacteria, Thiobacillus, the hydrogen, phenol, naphthalane, benzene, toluene, methene, heptane, naphthenic acid oxidizing bacteria, etc. The total number of bacteria reaches several million per ml of water. All the microflora actively digests the water soluble organic substances, and the range of ecological conditions for their development is quite extensive — a temperature ranging from 10 to 70 - 80°, with water mineralization up to 100 - 150 g/liter, or more.

Many investigations have shown that the microorganisms are capable of utilizing hydrocarbons of different classes of simple and complex structure, e.g., practically all of the hydrocarbons making up petroleum. In this case, the extensive prevalence of bacteria in waters of petroleum deposits under the conditions of absence of free oxygen convincingly confirms the possibility of anaerobic lysis of hydrocarbons with the formation of aliphatic acids [19].

To our view, the microbiological processes may explain the presence of aliphatic acids in subterranean waters, and a source for oxidation may be the hydrocarbons of the petroleum-gas deposits (in this case, the maximum amount of acids is observed), as well as the dispersed hydrocarbons of rock and the dissolved hydrocarbons of subterranean waters.

It is possible that a certain fraction of the volatile neutral compounds, such as the esters and alcohols, are also of microbiological origin.

Besides the microbiological formation of a number of organic compounds, processes of decomposition of organic compounds also occur in waters. Thus, the process of biochemical decomposition of carbohydrates to carbon dioxide, methane, and hydrogen is widespread.

Processes of anaerobic breakdown of aliphatic acids to propane and butane also occur in these waters.

Besides the microbiological processes, physico-chemical reactions also occur in subterranean waters: hydrolysis polycondensation, catalytic hydrogenation, acid carboxylation, etc. All of these lead to various conversions in the dissolved organic substances [3].

A statistical analysis of determining organic material in the subterranean waters makes it possible to note that the histograms of distribution of organic substances, in an overwhelming majority of cases, yield a j-shaped curve which is characterized by a symptotic approximation of the descending and ascending arms to the coordinate axes. In accordance with the geochemical interpretation of this curve given by M. Ye. Al'tovskiy [1], the j-shaped curve corresponds to regions of unstable concentrations of the initial accumulation of components of the chemical composition of subterranean waters.

The absence in all cases of a symmetrical single-peak curve which would have indicated, according to S. I. Smirnov [22], a condition of the material near physico-chemical equilibrium, confirms the presence of a non-persistent unstable state of the organic material in all types of subterranean waters. This instability is also characteristic for the waters of petroleum deposits, for which Smirnov demonstrated complete stabilization of the natural solution with respect to the ion-saline composition.

However, if one compares fluctuations in the variation factor (v) for the various indices of organic materials in waters of different groups, one can see its least changeability (and consequently the effect of the smallest number of factors) for the pre-edge waters of petroleum and gas-condensate deposits: 1) waters of gas-condensate deposits — v varies from 14 to 79; 2) the pre-edge waters of petroleum deposits — from 85 to 140; 3) waters of an unstressed region — 67 to 139; 4) ground waters — from 52 to 127; 5) waters of gas deposits — from 35 to 118; 6) post-edge waters of petroleum

deposits — from 59 to 147; 7) waters of nonproductive strata — from 29 to 118; 8) interstratal artesian waters — v varies from 45 to 151.

As is apparent from the given arrangement of groups of waters, the greatest changeability of the content of organic materials is characteristic for the deep waters outside petroleum deposits and for waters of petroleum deposits not in contact with them. From this, one may conclude that the greatest number of factors affects the formation of organic components of subterranean waters in deep water-bearing strata of the stratisphere. They may obviously be considered natural, since in this case the thermal factor and pressure begin to play a role, and the processes of interaction of water and rock proceed more actively, etc. In waters of regions that are unstressed, e.g., at the final stage in the history of the subterranean waters, the processes of formation of organic components stabilize. The same thing occurs in waters bounding the petroleum deposits, which are characterized by slowed water exchange, as a rule.

The above enables one to note that the general amount of organic substances in subterranean waters is extremely great and, on the strength of this, should not be omitted during the geochemical study of subterranean waters. Thus, if one does not take into account the maximum content of organic material in the edge waters of petroleum-gas deposits of limited extent, but takes the mean value of C_{org} concentration on the order of 50 mg/liter, then the amount of organic carbon in the subterranean waters of the 5 kilometer zone of the stratisphere alone (50 million km^3) comprises $2.5 \cdot 10^{12}$ tons. This quantity is comparable to the organic carbon contained in the World Ocean ($2 \cdot 10^{12}$ tons), in coal ($5 \cdot 10^{12}$ tons), in peat ($1 \cdot 10^{12}$ tons), and in the soil ($0.7 \cdot 10^{12}$ tons), and is exceeded only by the C_{org} content in sedimentary rocks ($3.5 \cdot 10^{15}$ tons).

References

1. Al'tovskiy, M. Ye. Gidrogeologicheskiye pokazateli neftegazonosnosti (Hydrogeological Indices of Petroleum-Gas Bearing). Moscow, "Nedra" Press, 1967.

2. Al'tovskiy, M. Ye., Z. I. Kuznetsova and V. M. Shvets. Obrazovaniye nefti i formirovaniye yeye zalezhey (The Formation of Petroleum and the Formation of Its Deposits). Moscow, Gostoptekhizdat, 1958.

3. Al'tovskiy, M. Ye., Ye. L. Bykova, Z. I. Kuznetsova and V. I. Shvets. Organicheskiye veshchestva i mikroflora podzemnykh vod i ikh znacheniye v protsessakh neftegazoobrazovaniya (Organic Substances in the Microflora of Subterranean Waters and Their Significance in Processes of Petroleum and Gas Formation). Moscow, Gostoptekhizdat, 1962.

4. Bars, Ye. A. and S. S. Kogan. Organicheskoye veshchestvo podzemnykh vod neftegazonosnykh oblastey (Metodika analiza i interpretatsii) [Organic Material of Subterranean Waters and Petroleum-Gas-Bearing Regions (A Method of Analysis and Interpretation)]. Moscow, "Nedra" Press, 1965.

5. Brodovskaya, A. A., Ye. L. Bykova and S. S. Frantskevich. The Two-Stage Method of Complete Determination of Organic Carbon in Natural Waters. ONTI-VIEMS, ekspress-insormatsiya, No. 26, Moscow, 1967.

6. Bykova, Ye. L., G. A. Goleva, A. A. Smirnova and I. N. Vorob'yeva. New Data in the Investigation of Organic Materials of Mineral Waters of the "Naftusya" Type. "Byul. MOIP", Geology Section, Vol. XLII, No. 3, 1966

7. Bykova, Ye. L. and I. B. Nikitina. The Interaction of Iron and Silicon with Organic Material in Natural Waters of Southern Yakutiya. Geokhimiya, No. 10, 1966.

8. Bykova, Ye. L., A. A. Brodovskaya and M. Ya. Dudova. Metody issledovaniya organicheskikh veshchestv podzemnykh vod (Methods of Investigating Organic Materials of Subterranean Waters). Moscow, "Nedra" Press, 1969.

9. Bykova, Ye. L., V. M. Shvets, I. K. Shilov and I. N. Vorob'yeva. The Significance of Water Soluble Organic Materials in the Formation of Iodobromine Waters. Sov. geologiya, No. 10, 1969.

10. Vernadskiy, V. I. Izbrannyye sochineniya, Vol. IV, "Kniga vtoraya. Istoriya prirodnykh vod" (Selected Readings, Vol. IV, Book 2. The History of Natural Waters"). Moscow, AN SSSR, 1960.

11. Germanov, A. I. and V. M. Panteleyev. The Organic Material of Subterranean Waters in Infiltrative Epigenesis. Izvestiya AN SSSR, ser. geol., No. 12, 1967.

12. Germanov, A. I. and V. M. Patenelyev. The Geochemistry of Hypergenic Migration of Copper in the Dzhezkazgan Ore Field. Geokhimiya, No. 3, 1970.

13. Zinger, A. S. Gazogidrokhimicheskiye kriterii otsenki neftebasonosnosti lokal'nykh struktur (na primere Nizhnego Povolzh'ya) [The Gas Hydrochemical Criteria for Estimating the Petroleum-Gas-Bearing Nature of Local Structures (Using the Example of the Lower Volga)]. Saratov University Press, 1966.

14. Kartsev, A. A. Osnovy geokhimii nefti i gaza (Fundamentals of the Geochemistry of Petroleum and Gas). Moscow, Nedra Press, 1969.

15. Kartsev, A. A., M. Ya. Dudova and O. P. Abramova. Organic Material in Rock Solutions. Izvestiya AN SSSR, ser. geol., No. 7, 1969.

16. Kissin, I. G., Ye. A. Bars, et al. Certain Data on the Effect of Elevated Temperatures on the Migration of Organic Material from Rocks to Aqueous Solutions. DAN SSSR, Vol. 189, No. 5, 1969.

17. Kononova, M. M. Organicheskoye veshchestvo pochvy (Organic Material of the Soil). Moscow, AN SSSR, 1963.

18. Metodicheskoye rukovodstvo po gidrogeologii dlya otsenki perspektiv neftegazonosnosti (A Methodological Manual of Hydrogeology for Assessing the Prospectives of Petroleum-Gas Bearing). Moscow, Gostoptekhizdat, 1961.

19. Rozanova, Ye. P. The Utilization of Hydrocarbons by Microorganisms. In the collection: Uspekhi mikrobiologii (Successes of Microbiology), No. 4. Moscow, Nauka Press, 1967.

20. Sbornik "Organicheskoye veshchestvo podzemnykh vod i yego znacheniye dlya neftyanoy geologii (Collection: The Organic Material of Subterranean Waters and Its Significance for Petrogeology). Moscow, VNIIOENG, 1967.

21. Skopintsev, B. A. and I. A. Goncharova. Uspekhi sovetskoy gidrokhimii v oblasti izucheniya organicheskikh veshchestv v prirodnykh vodakh. "Gidrokhimich. materialy" (Successes of Soviet Hydrochemistry in the Field of Studying Organic Substances in Natural Waters. "Hydrochemical Materials"). Vol, XLV, 1967.

22. Smirnov, S. I. Veroyatnostno-statisticheskiye zakonomernosti raspredeleniya khimicheskikh elementov v prirodnykh vodakh. Sb. "Gidrogeokhimich. materialy" (Probability-Statistical Principles of Determining Chemical Elements in Natural Waters. Collection: Hydrogeochemical Materials). Moscow, AN SSSR, 1963.

23. Starikova, N. D. Organicheskoye veshchestvo gruntovykh rastvorov Tikhogo okeana. V. kn.: "Khimiya Tikhogo okeana" (Organic Material of Ground Solution of the Pacific Ocean. In the book: Pacific Ocean Chemistry). Moscow, Nauka Press, 1966.

24. Surkov, V. N. Soderzhaniye organicheskikh veshchestv v mineral'nykh vodakh Severnogo Kavkaza. Sb. trudov prakticheskikh vrachey kurortov KMV (The Content of Organic Substances in Mineral Waters of the Northern Caucasus. A Collection of Transactions of Practicing Physicians of KMV Resorts), Vol. 6. Stavropol'sk. knizhn. izdatel'stvo, 1963.

25. Tyurin, I. V. Organicheskoye veshchestvo pochvy i yego rol' v plodorodii (Organic Material of the Soil and Its Role in Fertility). Moscow, Nauka Press, 1965.

26. Shvets, V. M. Certain Principles of the Prevalence of Organic Substances in Subterranean Waters. In the collection: Problems of the Geochemistry of Subterranean Waters. Tr. VSEGINGEO, nov. ser., No. 9, 1964.

27. Shvets, V. M. Organicheskiye veshchestva podzemnykh vod kak pokazateli neftegazonosnosti. V.sb. "Pryamyye metody poiskov nefti i gaza (Organic Substances of Subterranean Waters as Indices of Petroleum-Gas Bearing. In the collection: Direct Methods of Exploring for Petroleum and Gas). Moscow, Nedra Press, 1964.

28. Shvets, V. M., Z. I. Kuznetsova and T. P. Popova. Izucheniye organicheskogo veshchestva i mikroflory v podzemnykh vodakh. V kn.: "Sb. po gidrogeologii i inzhenernoy geologii (k 25-letiyu VSEGINGEO) [A Study of the Organic Material and Microflora in Subterranean Waters. In the book: Collection on Hydrogeology and Engineering Geology (For the 25th Anniversary of VSEGINGEO)], No. 22. Moscow, Nedra Press, 1969.